

Effects of Hydrogen Dilution and i-layer Thickness on a-Si:H Solar Cells Studied by Photoluminescence Spectroscopy

Guozhen Yue[1], Daxing Han[1], Jeffrey Yang[2], Kenneth Lord[2], Boajie Yan, and Subhendu Guha[2]

1. Department of Physics & Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3255
2. United Solar Systems Corp., 1100 W Maple Road, Troy, Michigan 48084

ABSTRACT

We use photoluminescence (PL) spectroscopy to characterize the effects of hydrogen dilution and i-layer thickness on electronic density of states in a-Si:H n-i-p solar cells that were prepared using plasma-enhanced CVD with no-, low-, standard, and high-H dilution. The PL shows two regimes: (I) Below the onset of microcrystallinity, a blue shift of the 1.4 eV PL peak energy and a decrease of the band width occur. (II) Above the onset of microcrystallinity, the PL efficiency decreases by a factor of 4-5, and the PL peak energy is red-shifted toward 1.2 eV as the μ c-Si volume fraction is increased. In addition, the solar cell open circuit voltage shows first an increase and then a decrease, correlating with the PL peak energy position. We conclude that the PL spectroscopy is a sensitive tool for characterizing the gradual a-to- μ c structural transition in thin film solar cells.

INTRODUCTION

The most stable, high-performance a-Si:H solar cells were obtained using a-Si:H prepared at a hydrogen-to-disilane dilution ratio just below the onset of microcrystallinity.[1] Recent experimental results indicate that an improved microstructure of the i-layer is responsible for the enhanced stability. Transmission electron microscope results suggested[2] that a-Si:H made with H dilution is a heterogeneous mixture of an amorphous matrix and more ordered linear-like objects. X-ray diffraction (XRD) demonstrated [3] that the width of the first diffraction peak is narrower in the most stable material, indicating improved medium-range order. On the other hand, due to the lack of sensitivity of Raman and XRD for obtaining crystalline silicon signals for very small fractions ($\sim 1\%$) and/or small crystallite sizes, a more sensitive technique is needed. Furthermore, the structure of these transition materials was found to be sensitive not only to H dilution but also to substrate surface and film thickness.[3,4] In this paper, we report results on a series of n-i-p solar cells made by plasma-enhanced chemical vapor deposition (PECVD) with varied H dilutions and i-layer thickness using PL spectroscopy.

EXPERIMENTAL RESULTS AND DISCUSSION

a-Si:H n-i-p solar cells were made by PECVD on stainless steel substrates. The reaction gas was either disilane or disilane diluted by hydrogen. Several dilution ratios, $R = 0.8, 1.0, 1.2$ and 1.6 were used, where $R=1.0$ is the standard H dilution ratio,[5] and $R=1.2$ and 1.6 represent 20% and 60% more H dilution, respectively. The i-layer thickness was

$d \approx 110, 220$, and 450 nm. Relevant cell deposition parameters, XRD results, and V_{oc} are listed in Table I. The sample was cooled to 80 K on a cold stage. A 632.8 nm laser beam of 100 mW/cm² was used to excite PL. The absorption depth of the 632.8 nm light in both a-Si:H and μ c-Si is greater than the cell thickness so properties of the bulk material are obtained. The PL spectra were analyzed using a grating monochromator equipped with a LN₂-cooled Ge detector.

Table I. Characteristics of solar cells prepared with different H dilution ratio (R) and thickness (d)

Sample No.	H-dilution		Thickness		XRD		V_{oc} (V)
	ratio R	d (nm)	FWHM (degrees)	μ c fraction (%)			
#583	1.0	130	6.4(± 0.6)	0			0.962
#591	1.0	220	5.3(± 0.3)	0			0.963
#569	1.0	450	5.43(± 0.15)	0			0.984
#592	1.2	105	5.1	0			0.955
#576	1.2	416	4.98	4			0.766
#593	1.6	110	4.5	~ 5			0.709
#579	1.6	220	4.1	27			0.529
#580	1.6	450	3.20	36			0.466

The PL spectrum at 80 K is dominated by the tail-to-tail transitions giving a PL main-band peaked at ~ 1.4 eV with FWHM ~ 0.3 eV, which depend on the optical gap and the width of the tail states, respectively.[6] A defect-band peaked at 0.8 - 0.9 eV is 3-4 orders of magnitude weaker than the main-band at low temperatures. More recently, a 1.0 - 1.2 eV PL band was found to be a characteristic feature of μ c-Si from a series of a- to μ c-Si transition samples.[7,8] We show the normalized PL spectra at 80 K in Figs. 1(a), 1(b) and 1(c). Let us first examine the three a-Si:H cells with $R=1.0$ in Fig. 1(a). When d is increased from 110 to 220 and then to 450 nm, the PL peak energy is blue shifted from 1.36 to 1.39 to 1.42 eV. At the same time, there is a low energy peak at ~ 1.2 eV for the thickest cell. Fig. 1(b) shows the PL spectra for the cells with $R=1.2$. The FWHM of the PL main-band decreased from 0.3 eV to 0.2 eV as the thickness increased from 105 to ≥ 215 nm. When $d=416$ nm, there is a μ c-Si volume fraction of 4% determined by XRD; and the PL features are: (a) the total PL intensity decreases by a factor of 4-5 compared to a-Si:H; and (b) there is no longer a blue- but a red-shift of the PL peak energy in addition to the 1.2 eV band. Fig. 1(c) shows the PL spectra for the three μ c-Si cells with $R=1.6$. One can see that as the thickness increases the low energy PL appears from a broad tail to a high shoulder and then dominates.

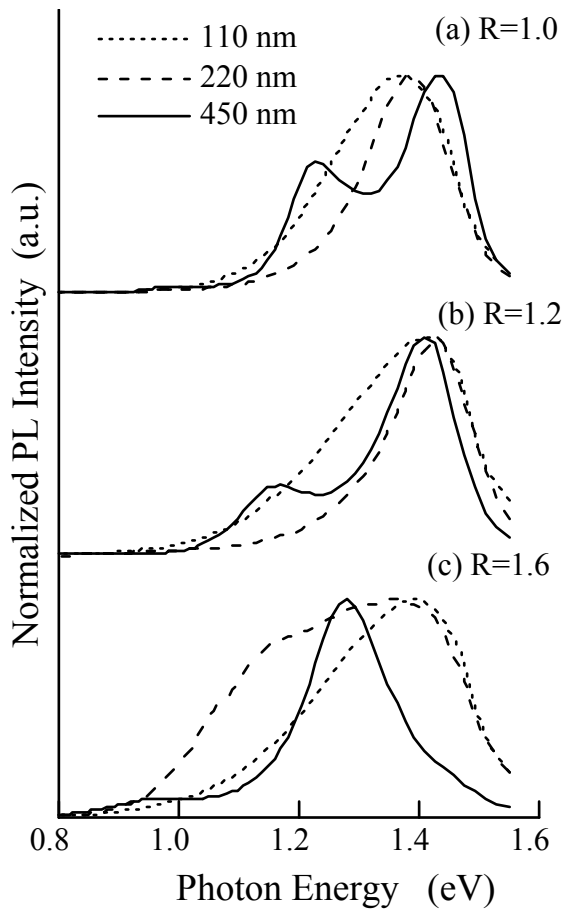


Fig. 1 PL spectra for three different i-layer thickness and H-dilution ratio of (a) $R=1.0$, (b) $R=1.2$, and (c) $R=1.6$.

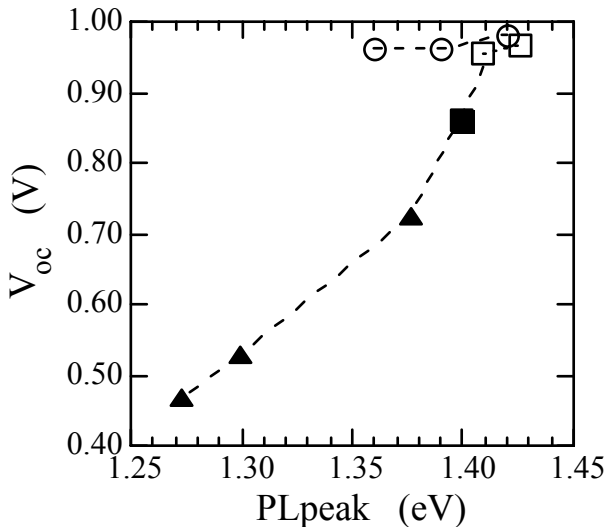


Fig. 2 V_{OC} as a function of the PLpeak. The open- and solid symbols represent the regimes in which V_{OC} increases as the PL is blue shifted and the V_{OC} rapidly decreases as the PL is red shifted, respectively.

SUMMARY

We have shown that the electronic density of states is significantly changed with both H dilution and film thickness in these transition samples. The features of the PL spectra characterize the gradual improvement of the a-Si:H network order and the transition to μ c-Si. Distinguished by the onset of microcrystallinity characterized by XRD, we found that there are two regimes of the PL features for the samples near transition. In the samples below the onset of detectable microcrystallinity, the dominant factor of increased H dilution and thickness is to improve the a-Si:H structural order. As a result, the PL peak energy is blue-shifted, and the linewidth is narrowed. In the samples above the onset of microcrystallinity, the main factor is an increase of the μ c-Si volume fraction, which results in the decrease of the total PL intensity and the increase of the 1.2 eV PL band. Meanwhile, the V_{OC} quickly decreases as the PL energy is red-shifted. Proper conditions such as a combination of H dilution ratio and thickness at $R=1.0$, $d=0.2-0.4 \mu\text{m}$ and $R=1.2$, $d=0.2 \mu\text{m}$ have produced the highest V_{OC} as shown in Table I. These are consistent with the most stable high-performance a-Si:H solar cells prepared just below the onset of microcrystallinity.[3]

ACKNOWLEDGEMENT

The work at the University of North Carolina and United Solar is supported by the National Renewable Energy Laboratory via subcontracts under the Thin Film Partnership, XAK-8-17619-11 and ZAK-8-17619-09, respectively. The XRD data are furnished by D. Williamson. G.Yue is partially supported by NSF-Int-9604915.

References

- (1) D.V. Tsu, B.S. Chao, S.R. Ovshinsky, S. Guha, and J. Yang, APL **71**, 1317 (1997).
- (2) R.J. Koval, J. Koh, Z. Lu, L. Jiao, R.W. Collins, and C.R. Wronski, APL **75**, 1553 (1999).
- (3) S. Guha, J. Yang, D.L. Williamson, Y. Lubianiker, J.D. Cohen and A.H. Mahan, APL **74**, 1860 (1999).
- (4) J.H. Koh, Y. Lee, H. Fujiwara, C.R. Wronski, and R.W. Collins, APL **73**, 1526 (1998).
- (5) J. Yang, K. Lord, and S. Guha, Mater. Res. Soc. Symp. Proc. **609**, (2000) (in press).
- (6) R.A. Street, *Hydrogenated Amorphous Silicon* (Cambridge University Press, 1991), Chaps. 4, 6-8; Adv. Phys., 30, 593 (1981).
- (7) Guozhen Yue, J.D. Lorentzen, Jing Lin, Daxing Han and Qi Wang, APL **75**, 492, (1999).
- (8) Guozhen Yue, Daxing Han, D.L. Williamson, Jeffrey Yang, Kenneth Lord and Subhendu Guha, APL **77**, 3185 (2000).